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Indian J. Phys. **68B** (6), 473 – 493 (1994)

I J P B
- an international journal

Atmospheric ozone, its depletion and Antarctic ozone hole

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Received 19 July 1994, accepted 7 October 1994

Abstract : In this paper, the information on ozone depletion and ozone hole at Antarctica is reviewed. Beginning with 1960's with the availability of new information on solar radiations from rocket-borne experiments, accurate information on stratospheric reaction rates and of ozone concentrations, it became clear that the atmospheric ozone concentration is less than that predicted before. Search for new destructive processes for O_3 was then made. Several catalytic reactions involving ozone were identified. It was further realised that Solar UV-B (3200–2800 Å) radiations are not totally absorbed by the ozone layer and the remaining part on coming to the ground, affects man, animals, fishes and plants. Thus, ozone depletion poses a serious problem. It has been learnt that the depletion of ozone is due to technological progress in rocketry, supersonic aircraft flight, refrigeration, nitrogeneous fertilisers and others.

Another problem of great concern to mankind was the dramatic decrease of O_3 concentration during Spring in Antarctica, reported in 1985. The decrease in ozone content was confirmed by using ground-based, balloon and satellite-borne instruments. It was further observed that ozone hole does not occur in Arctic region. Vigorous studies of ozone depletion in Antarctica were then made. Special meteorological features of Antarctic region are brought out and their differences in two polar regions are noted. Reactions for ozone depletion are formulated and theories are proposed for the hole. Till now, the problem is only partially understood. For complete information, continued work for many years is required.

Keywords : Ozone chemistry, upper atmosphere, collisional processes

PACS Nos. : 94.10.Fa, 94.10.Rk

Plan of the Article

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1. Introduction

Atmospheric ozone is a very minor constituent of the atmosphere. Its amount in the atmosphere is on the average only 2.5 mm reduced to S.T.P. It presented many exciting problems at different times in the course of last one hundred years. After the discovery of very strong absorption band of ozone in the ultraviolet region by Hartly in 1888, it become clear why there was a sharp cut-off of solar radiations at about 2900 Å as observed from the ground. Atmospheric ozone is present in the three regions of the atmosphere–troposphere, stratosphere and mesosphere and plays significant role in these regions. In the troposphere, although present only 10% of its total amount, it plays an important role of cycling minor species. In the region ahead, it contributes to warm stratosphere and in mesosphere it initiates many important reactions.

In late 1930's, it was shown that atmospheric ozone has photochemical origin and immediately after World War II micro-spectroscopists corrected the belief that structure-wise ozone is a long isosceles triangle having three O atoms at its ends (from the fact that an oxygen atom can be easily dissociated from an ozone molecule). It forms a triangle having a wide vertical angle of 116°.

The detection of depletion of atmospheric ozone in late 1960's, led to postulate several catalytic reactions. The involvement of NO_x in ozone chemistry causes about 60% and chlorine only a few percent of ozone destruction. Had ozone not been absorbed in the stratosphere, ultraviolet radiations from the Sun would have come to the ground and affected man, animals, plants and fishes very seriously. It considerably affects human beings, so much so, that many countries under the auspices of UNESCO resolved not to participate in activities which would seriously deplete ozone in the atmosphere. A careful watch on atmospheric ozone is made so that its level does not decrease below its critical level.

Again, the discovery of ozone hole in the Antarctic region is very exciting. Strangely enough, such hole is not observed in Arctic region. Balloon-borne and satellite-borne experiments were hurriedly undertaken. The meteorological conditions of the two polar regions were ascertained and explanations were put forward for ozone hole.

2. Solar rays cut-off at 2900 Å

The radiations from the Sun is incident copiously on the atmosphere, but only the wavelengths longer than 2900 Å reach the ground. The question arises : Is this cut-off due to the absorption of radiation in the solar atmosphere or by the terrestrial atmosphere?

The answer came in 1880 when spectroscopist Hartly showed that an allotropic modification of oxygen, the well-known ozone (O_3) molecule, strongly absorbs radiations shorter than 2900 Å and therefore prevents them from reaching the ground. A search for ozone in the atmosphere was then made. The first ozone measurement of the atmosphere by sounding balloons was made by father and son, E and VH Regener on June 26, July 7 and 31 of 1934. They showed that as the balloon rose, more ozone was left below and the spectrum recorded by a quartz spectrograph extended more towards the ultraviolet.

As a result of this and other experiments, a good amount of information on atmospheric ozone has been obtained as follows :

(i) Ozone is present mainly in stratosphere—from above tropopause to about 50 km with centre of mass at 25 km.

(ii) The amount of ozone is small, averaging about 2.5 mm at S.T.P. It represents about one-millionth of total atmospheric particles.

(iii) Its concentration varies from day-to-day, season-to-season and year-to-year.

(iv) Ozone concentration varies with altitude (Figure 1) and latitude (Figure 2).

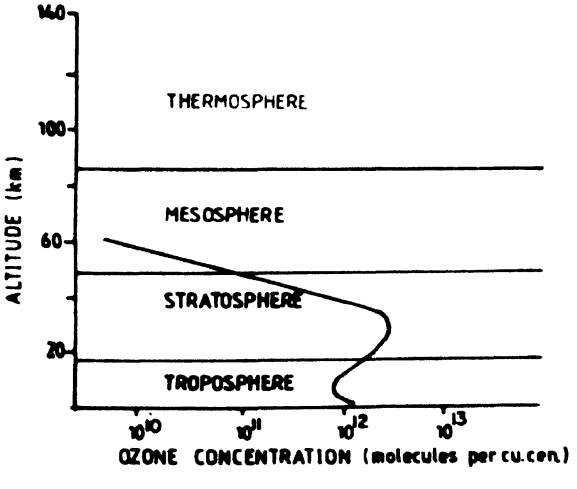

Figure 1. The variation of ozone concentration with altitude.

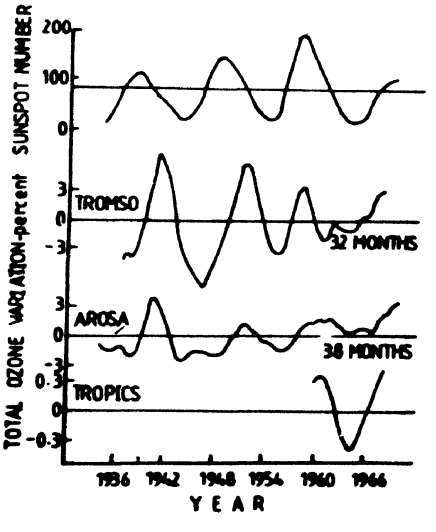

Figure 2. The variations of sunspot numbers at Tropics, Arosa and Tromso and also of ozone concentration. There is a lag between the two variations.

(v) Much greater variation in ozone level is observed over the Pacific Ocean than expected.

(vi) It is plentiful near the poles than at the equator.

(vii) It is abundant in winter compared to its summer value.

(viii) A significant amount of ozone is also produced in the troposphere.

(ix) There is a lag between the sunspot cycle and ozone concentration variations (Figure 2).

(x) Ozone has strong absorption starting from 2200 Å and ending near 2900 Å.

(xi) The ozone layer acts as a heat reservior in the middle atmosphere.

3. Formation of ozone in the primitive atmosphere

It is believed that the primitive terrestrial atmosphere was oxygenic in nature. O_3 was produced by photodissociation of water vapour as follows :

$$H_2O + h\nu \rightarrow OH + H$$

$$OH + h\nu \rightarrow O + H$$

$$O + O + M \rightarrow O_2 + M$$

$$O_2 + O + M \rightarrow O_3 + M$$

M is the third body which conserves energy and momentum of the reaction. Due to O_3 layer formation, solar UV radiations were absorbed and prevented from coming to the Earth's surface. As a result, photodissociation of water vapour was stopped. Later on, O_3 was formed by *different processes*.

4. Steady-state ozone concentration

In 1930, Sydney Chapman [1] postulated chemical reactions for the formation of ozone in the atmosphere, namely

(i) $O_2 + \text{UV light} \rightarrow O + O$
$(\lambda < 1750\ \text{A})$
$O + O_2 + M \rightarrow O_3 + M$

(ii) $O_3^* + O \rightarrow O_2 + O + O$
$O + O_2 + M \rightarrow O_3 + M.$

Ozone is formed in the excited state. The extra energy is transferred to other molecules in the surrounding atmosphere which is rapidly converted to heat. Thus, the production of ozone is accompanied by warming up of the stratosphere.

Ozone concentration does not continue to increase, as it is also destroyed by ultraviolet rays

$$O_3 + \text{UV light} \rightarrow O + O_2.$$

The oxygen atoms released from ozone destruction combine with O_2 molecules forming again ozone molecules. Since ozone is very reactive, an ozone molecule combines with an O atom producing two O_2 molecules

$$O + O_3 \rightarrow 2O_2.$$

Therefore, O_3 is constantly being created and destroyed by the action of solar UV radiations. Also O_3 may be removed by the reaction

$$O_3 + O_3 \rightarrow 3O_2.$$

The concentration of O_3 in the stratosphere increases with height and attains a maximum because O_2 density increases as the altitude is decreased, whereas the other building ingredient O atom density increases as the altitude is increased (Figure 1). Because of the effect of wind which carries ozone away from the equator, and by the action of Sun, the O_3 layer is closer to the surface of the Earth at the poles than at the equator.

The amount of ozone in the atmosphere, as calculated theoretically from the above reactions, namely one-millionth of atmospheric particles, was confirmed by experiments.

5. Other ozone processes

At this stage, scientists felt that the atmospheric ozone problem is fairly understood. The research in the field then was slowed down. Beginning with 1960's, new information on solar radiations became available from rocket-borne experiments. Also, accurate and increased information on stratospheric reaction rates and on direct measurements of ozone concentration were available. It was then realised that the steady state atmospheric ozone concentration is somewhat less than that predicted by Chapman's mechanism, indicating that in addition to loss processes considered before, some other reactions are at work for the destruction of ozone. That ozone decreases with time is also confirmed from the observations from satellites, which showed that the stratospheric ozone is decreased at the rate of 0.5% per year from 1970.

6. New destructive ozone processes

A search for new destructive processes for atmospheric ozone was then made. It was realised that Bates and Nicolet [2] had already suggested a catalytic reaction. This along with major ozone destroying processes are given below :

(i) Bates and Nicolet [2], (OH_x compounds)

$$\begin{aligned} OH + O_3 &\rightarrow HO_2 + O_2 \\ HO_2 + O &\rightarrow OH + O_2 \\ \hline O_3 + O &\rightarrow 2O_2. \end{aligned}$$

(ii) Paul Crutzen [3], (NO_x compounds)

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \\ NO_2 + O &\rightarrow NO + O_2 \\ O_3 + O &\quad\quad 2O_2. \end{aligned}$$

These reactions can also proceed by other pathways

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$$
$$N_2O_5 + H_2O \rightarrow 2HNO_3.$$

(iii) Molina and Rowland [4], (ClO_x compounds)

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$
$$\overline{O_3 + O \rightarrow 2O_2.}$$

These reactions can also proceed by other paths

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + ClO \rightarrow 2Cl + O_2.$$

(vi) McElroy *et al* [5], (BrO_x compound)

$$Br + O_3 \rightarrow BrO + O_2$$
$$BrO + O \rightarrow Br + O_2$$
$$\overline{O_3 + O \rightarrow 2O_2.}$$

These reactions show that OH_x, NO_x, ClO_x and BrO_x act as catalysts and hence small amounts of these compounds produce multiplying effects in removing atmospheric ozone.

7. Pollutants $NO–NO_2$ and Cl–ClO

The pollutants $NO–NO_2$ and Cl–ClO can enter the stratosphere either by direct release into the stratosphere or by releasing at the surface of the Earth from compounds which are then carried upwards and converted into these pollutants by solar radiations [6].

With regard to the entry of pollutant $NO–NO_2$, it may be noted that in late 1960's, plans were drawn for building supersonic transported (SST) aircrafts—the Anglo-French Concorde and Soviet Tupolev–144. The potential stratospheric ozone changes associated with such aircrafts are not by the supersonic velocity at which they fly but rather due to high altitudes for which their flights are designed. The Concorde and the Tupolev–144 fly at a height of more than 10 miles (Figure 3).

When air is heated to high temperature by the passage of SST aircrafts, some N_2 and O_2 molecules react to form NO and become ready to participate in the NO catalytic chain. Again, nitrogeneous fertilisers also produce $NO–NO_2$ which are trapped in the stratosphere.

As regards entry of the pollutant Cl–ClO, it may be mentioned that in 1974 Molina and Rowland [4] proposed that ozone is converted from liquid to gaseous state by CCl_3F (F–11)

and CCl_2F_2 (F–12), which are widely used as aerosol propellants and refrigerants, by the solar ultraviolet radiations at an altitude of 20 miles. They released abundantly Cl and ClO which afterwards participate in the catalytic reactions leading to ozone destruction (Figure 3).

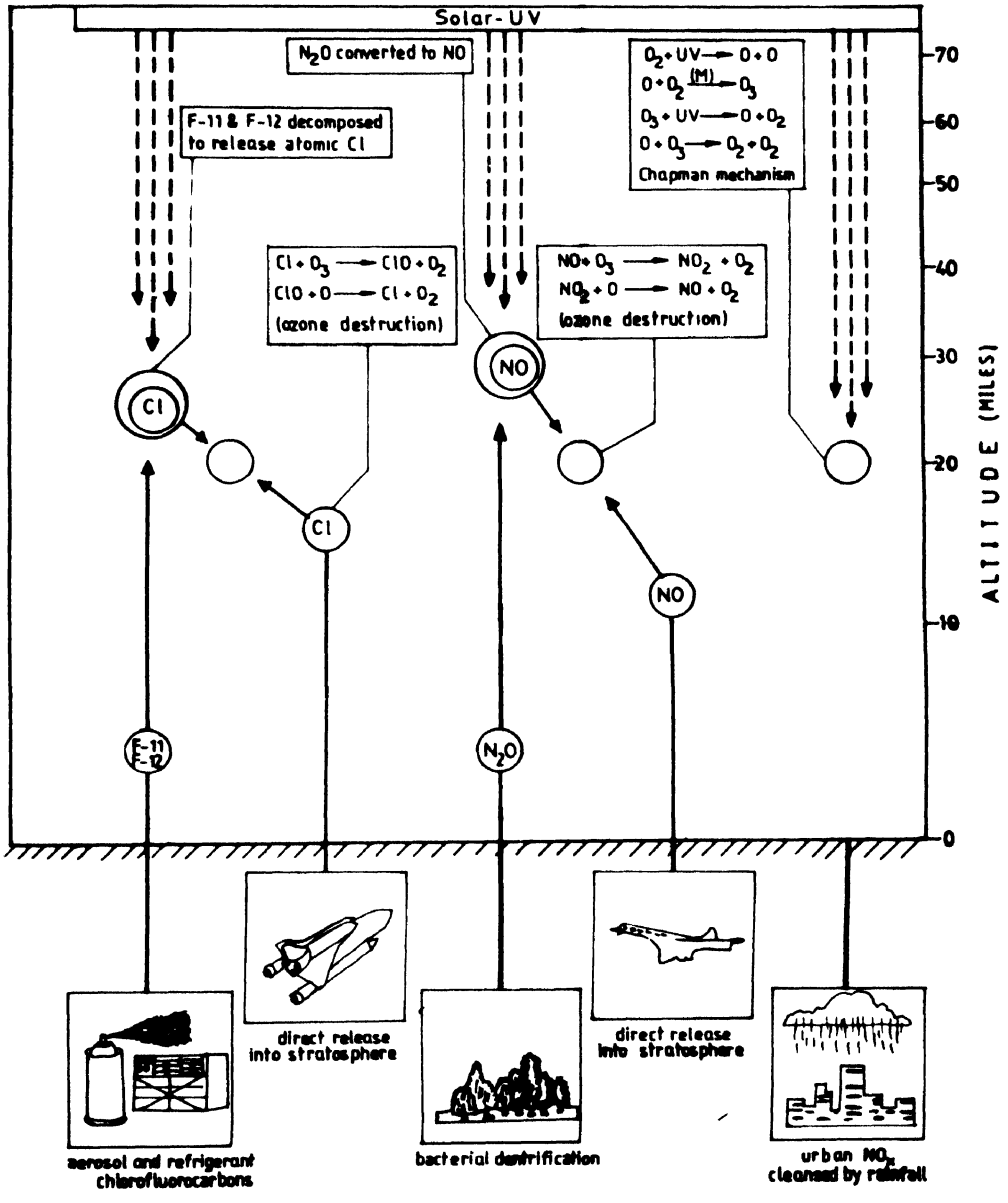

Figure 3. The ozone depletion due to different causes (By courtesy, Science and the Future 1979 Yearbook, Britannica Inc., Chicago).

It is to be noted that stratospheric pollutions are distributed throughout the globe and hence are international problems.

8. Effect of solar UV absorption by atmospheric ozone

Ozone absorbs solar ultraviolet radiations. The wavelength range 2000–2800 Å, known as the *UV–C region*, is lethal to man and living organisms and is *totally* absorbed by atmospheric ozone. Between 2800–3200 Å, called *UV–B region*, ozone absorbs *but not all* the radiations and is lethal to many forms of life. Ultraviolet radiation above 3200 Å, the *UV–A region*, is relatively harmless and is absorbed *only slightly* by atmospheric ozone (Figure 4). Hence, we are concerned only with UV–B radiations which affect man, animals, plants and fishes.

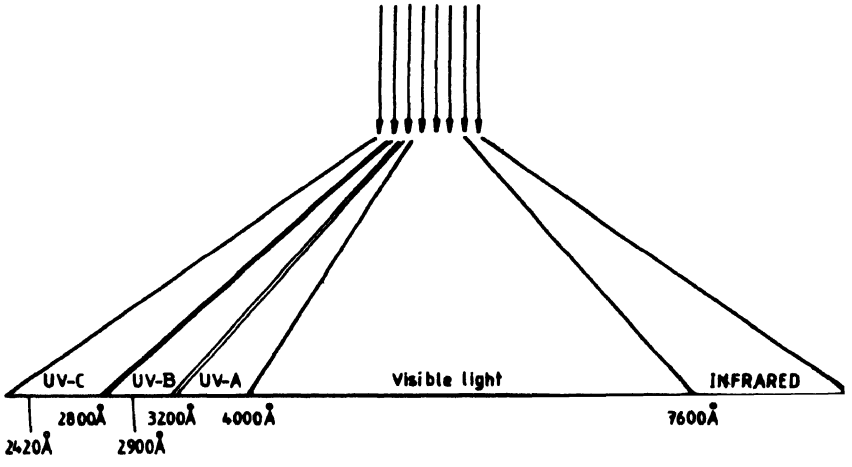

Figure 4. The UV–A, UV–B and UV–C regions in the solar ultra-violet radiations.

At the equator under clear skies, about 30% of the middle UV–B region of solar radiation is transmitted to the Earth's surface. Depending on the ozone level and cloudiness, the transmission drops to 10%. Even at high latitudes, summer exposure to UV–B differs by little amount from those at the equator.

Direct exposure to UV–B radiations damages both skin and eyes. Added exposure can increase the incidence of skin cancers and cataracts and suppress the immune system response. These radiations also age the skin prematurely. Exposure to UV–B causes stable retinal disorders, retinal degradation, visual aging and developmental disorder.

The correlation between the prevalence of various types of cataracts and flux of radiations varies with age. It has a larger effect among younger individuals. 0–1% depletion in ozone concentration can increase cataract prevelance by about 0.26%.

The sensitivity of aquatic organisms to small increase in UV–B is relatively small. Increase in these radiations involves potentially great risk. The level of these radiations striking sea, varies seasonally and with latitude.

Some of the important aspects of the impact of UV–B radiations due to ozone depletion on aquatic life are the following :

i. Based on DNA response, a 10% atmospheric ozone decrease would result in a 28% increase in biologically effective radiations.

ii. Because aquatic organisms are small and do not usually have fixed location, it is very difficult to obtain accurate data or model the system and verify results.

iii. Determination of UV–B exposures to aquatic system is more complex than for terrestrial ecosystems because of the variable attenuation of these radiations in winter.

iv. Various experiments have shown that UV–B radiations damage plants essential to marine food and larvae of fish, shrimp and crab.

v. While the limits of tolerance and exposure have not been precisely determined for organisms, estimates for a wide variety of aquatic organisms show their limits are essentially equal.

9. Control of ozone depletion

To control ozone depletion, the following methods may be adopted :

i. Legislative control to restrict the use of pollutants. The State of Oregon in USA has passed a law prohibiting the sale of F-11 and F-12 after March, 1, 1977 as aerosol propellant. The Canadian and Swedish Governments also announced similar laws.

ii. Selective regulation of the use of certain pollutants whose complete restriction would affect the society. For example, complete restriction of nitrogenous fertilizer would affect the agricultural production. The USA Federal legislation has appreciably reduced the manufacture of fluorocarbon and its release into the atmosphere. However, such restriction deals with only about the half of the global release.

iii. To measure regularly the ozone content in the atmosphere in order to keep a watch so that the depletion may not be appreciable.

Regular ozone observations :

Ozone concentration varies with space and time. Different methods are used for determining the total ozone content and its concentration at different altitudes. It is generally measured in Dobson Unit (DU), which is one-thousandth of a centimeter. Concentrations of ozone are measured in ozone partial pressure or ozone mixing ratio.

Ground-based observation :

Two bands of solar UV radiations are used for ground-based observations—one almost unaffected by ozone and the other strongly absorbed by ozone. Measurement of the ratio of intensities of these two bands allows one to calculate the amount of ozone through which the sunlight has been transmitted.

Satellite-borne experiment :

Satellite-borne instrument records backscatter on reflected solar UV radiations. Two instruments, Solar Backscattered UV instrument (SBUV) and Total Ozone Mapping Spectrometer (TOMS), are at work abroad for Nimbus-7 Satellites. SBUV provides

information of both total ozone and its distribution with altitude. Using TOMS the total ozone over the entire globe is mapped on a daily basis.

It is found that there is less chlorine oxide below 35 km and a greater increase with height than expected theoretically. NASA observed that from 1970 to 1979, there was a decrease of ozone at the rate of 0.5% per year and that it occurred at the height where the destructive effects of flurocarbon was found to occur.

10. Treaty to protect ozone layer

Ozone depletion may pose a serious problem to mankind. To combat it, on March 23, 1985 a convention which includes USA, USSR, India and other nations signed a treaty at Vienna under the aegis of United National Environment Programme to adopt legislation or administrative means to control, reduce, limit or prevent activities that affect the ozone layer.

11. Antarctic ozone hole

Farman *et al* [7] reported the dramatic decrease of O_3 concentration during spring in Antarctica from ground-based spectro-photometric observations at British Antarctic Survey Station, Halley Bay (Figure 5). The decrease in ozone was also observed by different nations

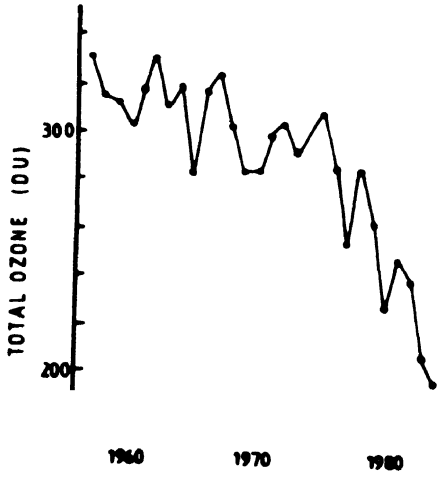

Figure 5. The decrease of O_3 concentration during spring as observed by Farman *et al* at the British Antarctic Service Station at Halley Bay.

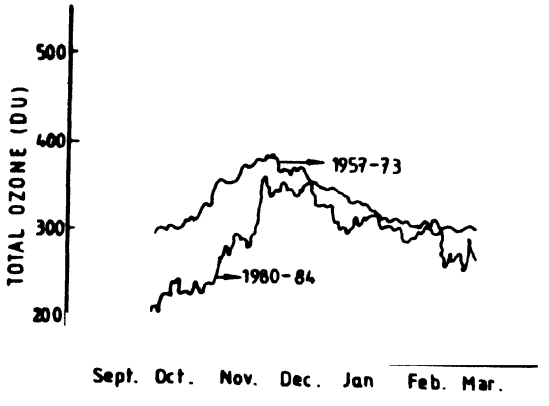

Figure 6. The daily mean values of atmospheric ozone at Halley Bay, the upper curve being the mean values for 16 seasons between 1957–1973 and the lower curve the mean value for 4 seasons in 1980–1984.

using ground-based balloons and satellite-borne instruments (Figure 8). The investigations are enlisted below :

Investigator	*Information obtained*
Farman *et al* [7]	It was the first report about the decrease of O_3 concentration (ozone hole), during spring at Antarctica. The observations were taken by ground-based spectrometer at British Antarctic Survey Station,

Halley Bay (76°S, 27°W) during 1957–84 (Figure 6). Monthly mean October values of ozone decrease by considerable amount (30–40%) from 1977, whereas monthly mean February values fluctuate within narrow limits (Figure 7). This report was afterwards confirmed by different investigators. It was shown that ozone hole is not localised at Halley Bay but extends over the Antarctica continent.

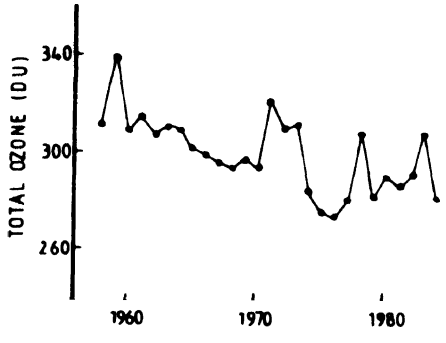

Figure 7. The monthly mean values of total atmospheric ozone at Halley Bay for February.

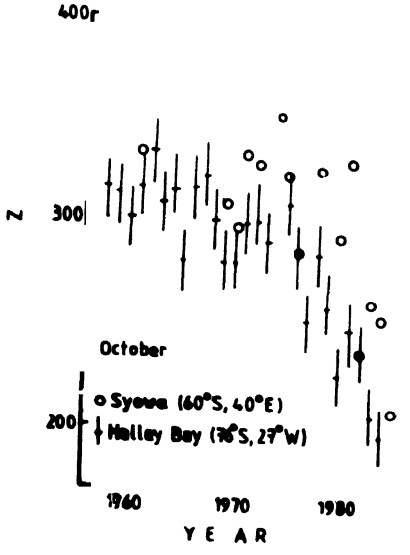

Figure 8. The total ozone variations in October at Halley Bay (76°S, 27°W) and Syowa (60°S, 40°E) for the period 1957–1984.

Stolarski *et al* [8] Performed SBUV and TOMS measurements on board the Nimbus-7 Satellite during 1979–85 and observed that the October minimum ozone is not located over a fixed area of Antarctica but changes its position and shape from day-to-day.

Hofmann *et al* [9] Performed balloon-borne measurement and observed that the total ozone declined by 35% while the integrated ozone between 14 and 18 km by 70%. Depletion within the vortex was as great as 90%.

Iwasaka [10] Performed ozonesonde measurements and observed that the ozone depletion was striking between 10–25 km (Figure 9). Temperature drop in the region was observed in spring only and reached frost point temperature in October-November, 1985 (Figure 10).

Aikin and McPeters [11] Performed SBUV measurements on Nimbus-7 Satellite and observed that ozone is 50% less at 18 km than the average surrounding ozone; at 50 km ozone is 20% less than the surrounding ozone field.

Komhyr *et al* [12] Performed measurements by spectrometer and observed 40% depletion of O_3 between 12–21 km.

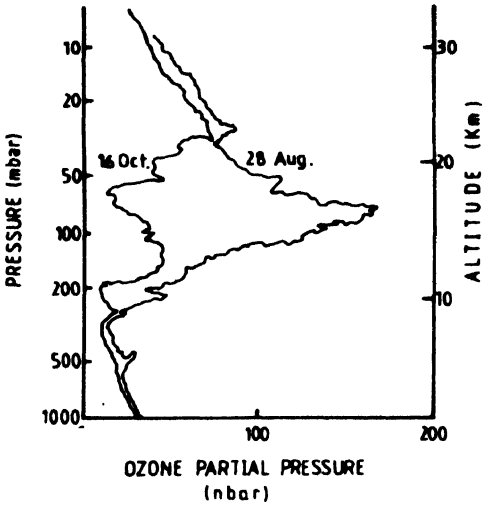

Figure 9. The atmospheric ozone partial pressure profiles at the beginning of ozone hole formation and at the height of depression

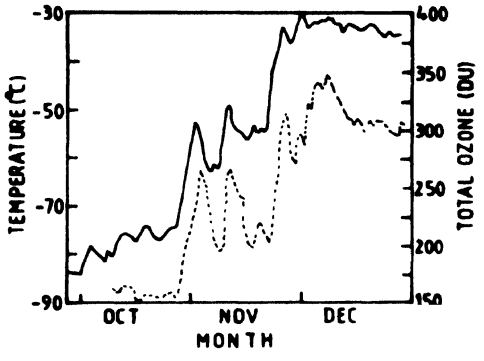

Figure 10. The correlation between the temperature (full line curve) and total ozone variations (dashed curve) at Antarctica.

Kruger *et al* [13] Performed TOMS measurements on board of Nimbus-7 Satellite and observed downward trend of October ozone value.

Gardiner [14] Performed balloon-borne experiments, and observed that depletion starts from late August and produces deep minimum in mid-October.

Schoeberl and Kruger [15] Observed dramatic year to year decline in total ozone over Antarctic in spring. There was no clear link between man-made pollutants and ozone depletion.

Sahai *et al* [16] Presented a comparison of the monthly ozone values in relation to other South American and Antarctic stations. Measurement of total atmospheric ozone was started in 1974 at Cachoerra Paulista (22.7°S, 45.0°W), SP, using a Dobson spectrometer. In 1978, another station was added at Natal (5.8°S, 35.2°W) RN, in collaboration with the National Oceanic and Atmospheric Administration, Boulder, USA (Figure 11). It was shown that the Antarctic ozone-decline does not extend to the middle and low latitudes.

Solomon *et al* [17] Showed from balloonsonde ozone data that ozone-changes are largely confined to the region from about 10 to 20 km during August to October.

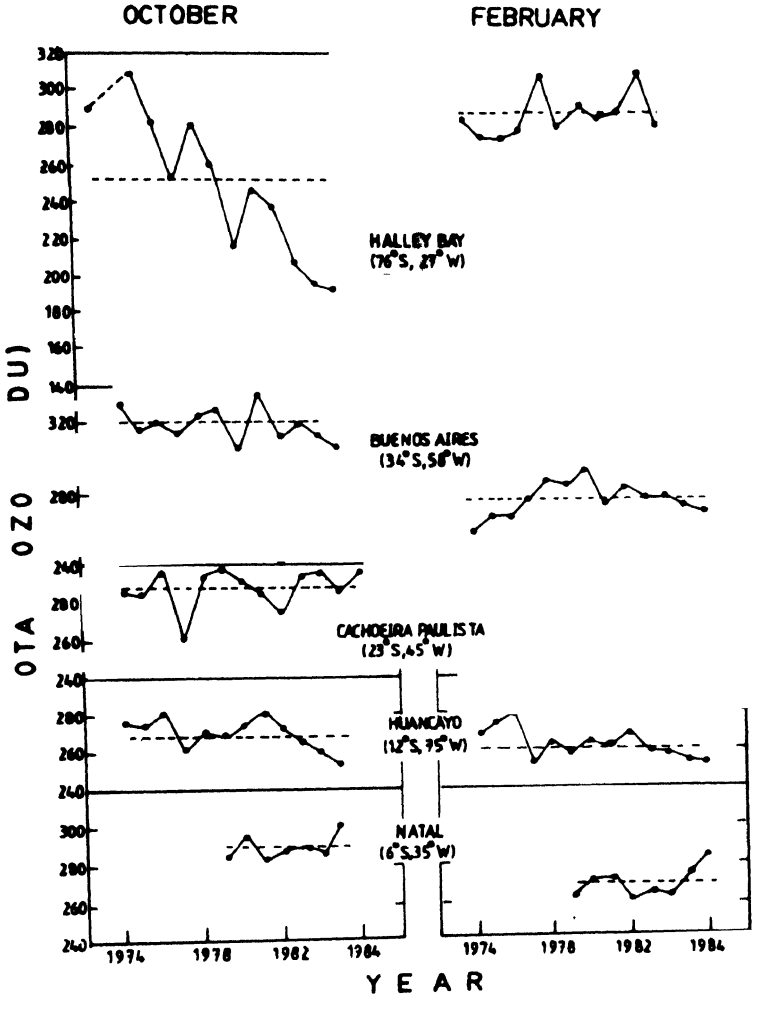

Figure 11. The variations of total ozone in October and February at Halley Bay and different stations in South America.

Stephenson *et al* [18]

Examined the depletion of stratospheric ozone caused by reaction of ozone with nitric oxide generated by energetic solar photons associated with solar flares. Chlorine acts as a catalyst. Ozone depletion takes place over a much larger area. They also concluded that the influence of solar photons on atmospheric ozone concentrations should not be ignored.

12. Special features of antarctic region

(i) In the polar region, both north and south, stratosphere starts from a relatively lower altitude of 8 km and then attains maximum ozone concentration between 15 and 20 km altitude.

(ii) Both the polar regions experience many weeks of continuous darkness. Antarctica experiences polar night during winter from May to August.

(iii) The temperature of the stratosphere at 50 mb pressure over Antarctica during winter drops to –80°C, which is nearly 20° to 30°C lower than the corresponding value over Arctic region [19]. At this low temperature, aerosols in the stratosphere form clouds

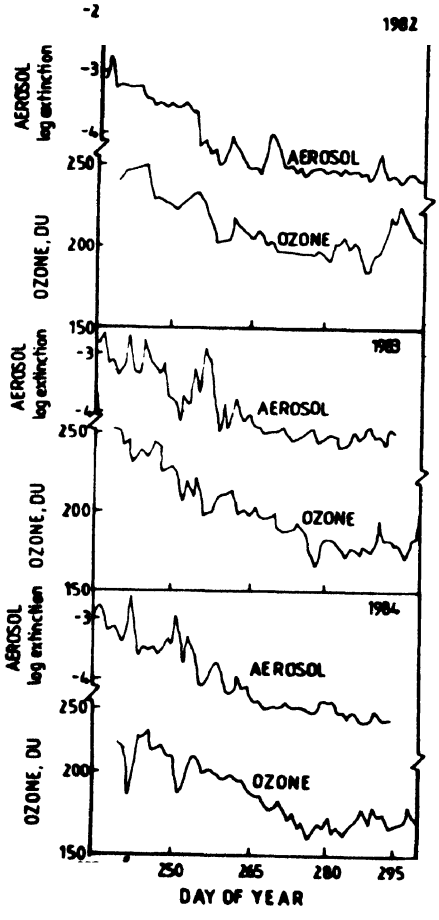

Figure 12. The variations of aerosol and ozone concentration in Antarctica.

between 10–20 km which is known as the Polar Stratospheric Clouds (PSCs). They are man-made non-reacting chemicals which stay in the atmosphere for over 100 years. When transported upwards in the stratosphere, they are broken up by ultraviolet light and produce active chlorine compounds (Cl and ClO) which destroy ozone molecules (Figure 12). PSCs clouds disappear in early November following the rise

of temperature. The formation of PSCs is more frequent in Antarctic than in Arctic region.

(iv) Due to chemical reactions occurring in PSCs, *inactive* form of chlorine is converted into *active* form and tie up some nitrogen compounds which normally serve as buffer. The active chlorine is released in a denitrified stratosphere. The balance between active and inactive forms of chlorine in the stratosphere determines how much ozone is destroyed. Bromine containing compounds have similar ozone destroying effect.

Measurements of ozone from aircraft by NASA during the Antarctic spring of 1987 showed high levels of ClO coinciding with low ozone. These measurements should that the Antarctic spring ozone hole was caused by active chlorine or bromine.

(v) There are differences between temperature and circulation patterns over the Arctic and Antarctic. Compared to Antarctic region which is relatively well understood, many aspects of what happen in the Arctic are uncertain. Stronger ozone-decline can be expected in Antarctic as a result of increased concentration of chlorine and bromine.

(vi) The polar vortices are usually centred over eastern Antarctica. They are more intense due to low temperature and strong winds, and stable than its Arctic counterpart. The Antarctic polar vortices do not breakdown before spring and are probably related to stratospheric warming.

(vii) Meteorological conditions of Antarctica is different from those of Arctic region. The extremely cold temperature (–80°C and lower) which occurs in the polar stratosphere region in winter allows polar clouds to form. Chemical reactions in the cloud droplets and other aerosol surfaces convert inactive chlorine to active forms and tie up some nitrogen compounds which normally serve as buffer. The active chlorine released in a denitrified stratosphere rapidly depletes ozone in the presence of sunlight.

13. Some other observations of ozone depletion

Investigator	Stations	Period of observation	Observed characteristics	Conclusion
Komhyr *et al* [20]	Southpole Antarctica	1964–1985	Mean monthly ozone	Largest mean monthly ozone decrease during Oct. and Nov; Autumn and winter months also exhibit decrease. Ozone increases lightly during February.
Gardiner and Shanklin [21]	Halley Bay Antarctica		Total ozone depression	Confirmed spring ozone depression
"	"	Dec. 1985 to Feb. 1986	Ozone density	Summer ozone density remains marginally lower than in the past

Contd.

Investigator	Stations	Period of observation	Observed characteristics	Conclusion
Angell [22]	Antarctica	1965–1985	Smoothed seasonal temperature variations at 100, 50 and 30 mb and smoothed seasonal total ozone deviation	Almost same type for the two variations
"	Antarctica and Stratosphere		Seasonal total ozone and low stratospheric temperature variations	In-phase relation between the two variations
Hofmann *et al* [23]	Mc.Murdo, Antarctica		Pressure (mb) against ozone partial pressure (nb) and ozone volume mixing ratio	Ozone partial pressure is maximum at a particular pressure. Pressure (mb) and ozone volume mixing ratio follow nearly same trend
Keys and Johaston [24]		1983	Geopotential thickness, total ozone and column of NO_2	Nearly same type of variation. There is an in-phase relation between the geopotential thickness peaks and those of total ozone and NO_2 column.
McCormick and Larsen [25]		Two days : Oct. 13, 1981 and Oct. 13, 1985	Simultaneous measurements of O_3, NO_2 and aerosol extinction with stratospheric aerosol and gas experiment in high latitude southern spring time.	NO_2 is strongly linked as O_3. Relative change in NO_2 across the vortex tends to follow that of O_3.
			Total column ozone amounts of O_3, NO_2 and aerosol optical depth	
Hamill *et al* [26]		Aug.–Oct. for 1982–1989	Total ozone column density as a function of time and comparative study with aerosol extinction at Antarctica	Ozone hole develops and clouds dessipate in the same place and time
Mahlman and Fels [27]		Each Oct. of 1979–1985	TOMS total ozone of minimum monthly mean value against the minimum value of Oct. monthly mean 30 mb temperature	Deep ozone minimum of the later years are associated with colder temperatures. Correlation between temperature and ozone data is +0.59. Dynamical mechanism may play important role in producing observed ozone-drops. Observed 10 DU drop in ozone per °C fall of temperature in polar vortex
Sekiguchi [28]	Soya (Japan)		Year to year change of monthly total ozone amount	Observed very high correlation between monthly mean ozone values and stratospheric temperature, O_3 concentration decreases with the decrease of temperature.

14. Suggested reactions for ozone depletion

Farman *et al* [7] suggested that the dramatic decrease of O_3 may be due to the reactions :

$$ClO + NO \rightarrow Cl + NO_2$$
$$Cl + O_3 \rightarrow ClO + O_2.$$

These reactions are important at low temperature of Antarctic spring. They also showed that the reaction can influence ozone concentration near 30 km.

Soloman *et al* [29] proposed the following catalytic cycle for the destruction of O_3 at lower altitudes :

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$HO_2 + ClO \rightarrow HOCl + O_2$$
$$HOCl + h\nu \rightarrow OH + Cl$$
$$2O_3 \rightarrow 3O_2$$

Soloman *et al* [29] showed that homogeneous chemistry could not explain observed O_3 depletion. PSCs clouds of Antarctica provided a reaction site for heterogeneous reactions. Such reactions between HCl and $ClONO_2$, H_2O and $ClONO_2$ were explored for possible mechanisms to explain the ozone depletion. They proposed that chlorine can destroy ozone catalytically in the Earth's atmosphere through the following reaction which has been mentioned before.

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$
$$O + O_3 \rightarrow 2O_2.$$

At lower altitudes, they also proposed the following catalytic cycle :

$$CH + O_3 \rightarrow HO_2 + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$HO_2 + ClO \rightarrow HOCl + O_2$$
$$HOCl + h\nu \rightarrow OH + Cl$$
$$2O_3 \rightarrow 3O_2.$$

The depletion of O_3 due to increasing levels of atmospheric chlorine maximises near 40 km where much of the available chlorine resides as ClO and Cl. At lower levels, these catalytic free radicals are effectively converted to the 'reservoir species', HCl and $ClONO_2$,

which are inert towards ozone. If densities of the catalytic species in the lower stratosphere are appreciably enhanced, both HCl and $ClONO_2$ are severely reduced by the reaction

$$HCl + ClONO_2 \rightarrow HNO_3 + Cl_2.$$

Cl_2 photolyses rapidly in the atmosphere and produces Cl which depletes O_3 concentration.

Another heterogeneous reaction which is similar to the above reaction was also proposed by them.

$$H_2 + ClONO_2 \rightarrow HNO_3 + HCl.$$

Solar photons of energies > 10 MeV enter the stratosphere at high geomagnetic latitudes (> 60°) and can penetrate to altitudes where ozone is most abundant [18]. Crutzen *et al* [30] showed that protons produce secondary electrons of energies 10 eV, which ionize and dissociate molecular nitrogen leading to the formation of nitric oxide. The nitric oxide can then play important role in ozone depletion through the following catalytic reactions :

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow NO + O_2.$$

15. Proposed theories for ozone hole

Several theories have been proposed for the depletion of ozone in Antarctic causing an ozone hole, as given below :

(i) Chemical theory :

Due to the chemical reactions occurring in polar stratospheric clouds which are formed in Antarctica from extremely cold temperature (–80°C and lower), *inactive* form of chlorine is converted into *active* form and ties up some nitrogen compounds which normally serve as a buffer. CFCs (choroflurocarbons) is proposed for the destruction of O_3 in Antarctica.

$$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl \qquad (\lambda < 230 \text{ nm})$$

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl \qquad (\lambda < 230 \text{ nm}).$$

The active chlorine released in a denitrified stratosphere rapidly depletes ozone in the upper stratosphere. The differences between both temperatures and circulation patterns over Arctic and Antarctic, are reflected in different ozone losses in the two regions.

(ii) Natural theory :

(a) Due to sunspot cycle

This theory is related to the sunspot cycle. The odd nitrogen levels are related to the 11-year solar cycle and are increased during solar maximum. Spring-time minimum in Antarctic ozone is principally due to the catalytic destruction of ozone by high level total nitrogen which are transported to the lower level from upper stratosphere and lower mesosphere.

(b) Due to volcanic eruption

Volcanic eruption is proposed for the formation of ozone hole. EI Chichon (Mexico) eruption in 1982 depleted Antarctic stratospheric ozone directly by the release of chlorine and indirectly by accumulation of released aerosol which provided larger area for heterogenous reactions. An alternative explanation is that the released aerosols or fine particles absorbing radiations, heating the stratosphere and causing a fountain-like movement of ozone-rich air up and out of the region.

It may however be pointed out no experimental evidence has been found in favour of the theory related to the sunspot cycle. Volcanic eruption has disappeared by now, but still ozone level is decreasing.

(iii) Dynamical theory:

According to this theory, ozone is not destroyed but only redistributed. Stratospheric ozone formation is due to solar radiations $\lambda < 242$ nm. Most of the ozone formation takes place over equator and at the top of the stratosphere. The air in this region tends to circulate from high to lower altitudes in the polar region and the newly-formed ozone is carried with it. The stable Antarctic polar vortex impede the ozone-rich air moving further southward until late in the spring. The stable polar vortex is an unique meteorological feature of Antarctica which only breaks down in mid-October due to rapid rise of stratospheric temperature at the appearance of sun. The ozone concentration starts increasing. As polar vortex is not stable in Arctic region, O_3 depletion does not occur.

Other theories have also been proposed. Experimental evidence favours chemical theory. However, the role of dynamical process in the formation of ozone hole cannot be ruled out. More observations are needed to decide the precise mechanism of the formation of ozone hole.

Man is now concerned with the depletion of ozone which is exceedingly important to mankind and living beings. At the same time he learns painfully that the depletion is due to bad effect inherent to technological progress in rocketry, supersonic aircraft flight, refrigeration and nitrogeneous fertilizer and others.

Man also learnt in 1985 [7] with profound concern the Antarctic ozone hole during spring. Vigorous scientific studies immediately followed. A great many observations were taken by ground-based, rocket and satellite-borne experiments. Theories are proposed, but the problems are now only partially understood and require continued work for understanding in fuller details.

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